



A systematic study of well-known electrolyte additives in LiCoO₂/graphite pouch cells

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HIGHLIGHTS

- Over 55 combinations of additives are studied in LiCoO₂/graphite pouch cells.
- High precision coulometry and impedance spectroscopy were used in these studies.
- The studies identify which additives give cells with the smallest parasitic reactions and the lowest resistance surface films.
- Electrolytes with 2% vinylene carbonate are a good baseline to compare advanced electrolytes against.
- Additives including VC, FEC, VEC, LiBOB, LiTFSI and others are highlighted in this work.

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ABSTRACT

The effectiveness of well-known electrolyte additives singly or in combination on LiCoO₂/graphite pouch cells has been systematically investigated and compared using the ultra high precision charger (UHPC) at Dalhousie University and electrochemical impedance spectroscopy (EIS). UHPC studies are believed to identify the best electrolyte additives singly or in combination within a short time period (several weeks). Three parameters: 1) the coulombic efficiency (CE); 2) the charge endpoint capacity slippage (slippage) and 3) the charge transfer resistance (R_{ct}), of LiCoO₂/graphite pouch cells with different electrolyte additives singly or in combination were measured and the results for over 55 additive sets are compared. The experimental results suggest that a combination of electrolyte additives can be more effective than a single electrolyte additive. However, of all the additive sets tested, simply using 2 wt.% vinylene carbonate yielded cells very competitive in CE, slippage and R_{ct} . It is hoped that this comprehensive report can be used as a guide and reference for the study of other electrolyte additives singly or in combination.

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1. Introduction

Extending the lifetime of Li-ion cells to 10–30 or even 50 years is one of the most challenging problems remaining to allow Li-ion batteries to be used in long life applications. Only a few papers [1,2] have presented experimental data describing lithium-ion cells cycled for years. Additionally, we are unaware of any tests on Li-ion cells that have lasted more than 22 years, given that the first Li-ion cells were produced in 1991 [3].

Two main approaches to extend the lifetime of Li-ion cells are the development of new electrode materials and electrolyte additives. The use of electrolyte additives is one of the most economic

and effective ways to improve the properties and performance of lithium-ion batteries [4,5]. For example, vinylene carbonate (VC) is one of the most studied electrolyte additives for lithium-ion batteries [6]. Aurbach et al. [7] studied VC in the graphite/Li, LiMn₂O₄/Li and LiNiO₂/Li half cells by comparing half cells with and without VC in a 1:1 mixture of ethylene and dimethyl carbonate with 1 M LiAsF₆. The irreversible capacity was reduced and the cyclability, especially at elevated temperatures, was enhanced for the graphite/Li half cells due to the addition of VC [7]. Aurbach et al. also demonstrated [7] that the addition of VC can help reduce the impedance of LiMn₂O₄/Li and LiNiO₂/Li half cells, respectively. Profatilova et al. [8] showed that the addition of fluoroethylene carbonate (FEC) can help increase the CE, increase the discharge capacity and reduce the impedance of the LiCoO₂/graphite coin cells in ethylene carbonate: ethyl methyl carbonate (EC:EMC, 3:7 vol.% ratio) with 1 M LiPF₆, compared to cells without FEC. Lu et al. [9] demonstrated the beneficial effect of lithium bis(oxalate)

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borate (LiBOB) as an electrolyte additive for the graphite/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ pouch cells in 1.2 M LiPF₆/EC/PC/DMC (1/1/3) electrolyte due to increased capacity retention from 87 to 96% at elevated temperatures, compared to the cells without LiBOB. Electrolyte additives have played and will continue to play an important role in the development of improved lithium-ion cells.

A systematic comparison of the effects of the most well-known electrolyte additives used in Li-ion cells is not available in the literature. Most reports showed that the addition of a certain electrolyte additive was beneficial to a specific lithium-ion cell type by comparing to results on cells without electrolyte additives. There is scarce data available that compares different additives and additive blends “head-to-head” on the same Li-ion cell type, however some limited reports exist [10–12]. Moreover, the impact of additives differs when different electrode materials are used [10].

Our research group has developed high precision coulometry as a method to screen the impact of electrolyte additives on cell lifetime [13,14]. These studies have established the need for extremely reproducible cells which only differ in the electrolyte additives used in order to measure the small differences in CE and slippage caused by various additives. Such reproducible cells are preferably machine-made by battery manufacturers. One of our recent studies involved 9 different electrolyte additives in various combinations in a study involving 160 Li[Ni_{1-x-y}Mn_xCo_y]O₂/graphite cells [15]. That work again demonstrated the link between increased CE and longer lifetime for cells with common electrolyte additives. However, the work was frustrating for the university authors because five of the nine electrolyte additives were proprietary and not disclosed. Some of these proprietary additives and their blends turned out to yield the best cells! In order to avoid further frustration for ourselves and the readers of our papers, links with manufacturers of Li-ion pouch cells have been established. These machine-made pouch cells are sent to us sealed, but dry, without electrolyte, and then they are filled with electrolytes containing additives of our choice at our facility. This protocol allows high quality results for a huge variety of electrolyte additives (limited only by our testing capacity) to be collected in a fully consistent manner.

This report compares well-known as well as borate additives in LiCoO₂/graphite pouch cells. The base electrolyte to which additives were added was 1 M LiPF₆ in ethylene carbonate: ethyl methyl carbonate (EC:EMC, 3:7 wt.% ratio, BASF), called the “control” electrolyte here. The 60-channel ultra high precision charger (UHPC) at Dalhousie University, which can measure the coulombic efficiency (CE) to an accuracy of $\pm 0.003\%$ [14], was used for these measurements. Electrochemical impedance spectroscopy measurements were also made at the end of the high precision charger experiments because reference [15] showed the importance of simultaneously maximizing CE and minimizing charge transfer impedance to create the longest lived cells.

Ceder [16] has developed the “materials genome” where the properties of materials have been computed using high throughput computational methods. The same researchers are now proposing to develop an “electrolyte genome”. To be useful, this electrolyte genome must consider the impact of electrolyte additives and high quality data, like that presented here, will be required for comparison to theory.

2. Experimental

Machine-made dry LiCoO₂/graphite pouch cells (402030 size, 200 mAh) were supplied by a reputable manufacturer (Obtained from Pred Materials Co., 60 East 42nd Street, Suite 1456 New York, NY 10165) and were filled and sealed at Dalhousie University. The graphite electrodes (synthetic graphite) consisted of a double sided graphite-coated copper strip of about 20 cm \times 2.3 cm with a

loading of 10 mg cm² on each side of the foil. The positive electrode consisted of a double sided aluminum LCO-coated strip of about 18 cm \times 2.2 cm with a loading of 22 mg cm² on each side of the foil. Fig. 1 shows SEM images of the fresh electrodes taken from a dry cell. Fig. 1a shows that the graphite particles are in the 10–30 μ m size range. No binder of carbon black is obvious in Fig. 1a. Fig. 1b shows an SEM image of the LCO electrode. The LCO particles are in the 5–10 μ m size range. Carbon black is visible in the LCO electrode.

Vinyl ethylene carbonate (VEC, BASF, 99.9%, water level less than 100 ppm), vinylene carbonate (VC, BASF, 99.97%, water level less than 200 ppm), lithium bis(oxalato) borate (LiBOB, Chemetall, water content less than 100 ppm), fluoroethylene carbonate (FEC, BASF, 99.94%), trimethoxyboroxine (TMOBX, BASF, purity not available), tris (trimethylsilyl) borate (TMSB, TCI America, 97%), triethyl borate (TEB, Sigma–Aldrich, 99%), trimethyl borate (TMB, Sigma–Aldrich, 99%), tri-tert-butyl borate (TtBB, Sigma–Aldrich, 99%), tributyl borate (TBB, Sigma–Aldrich, 99%) and trisopropyl borate (TiPB, Sigma–Aldrich, 98%) were used as electrolyte

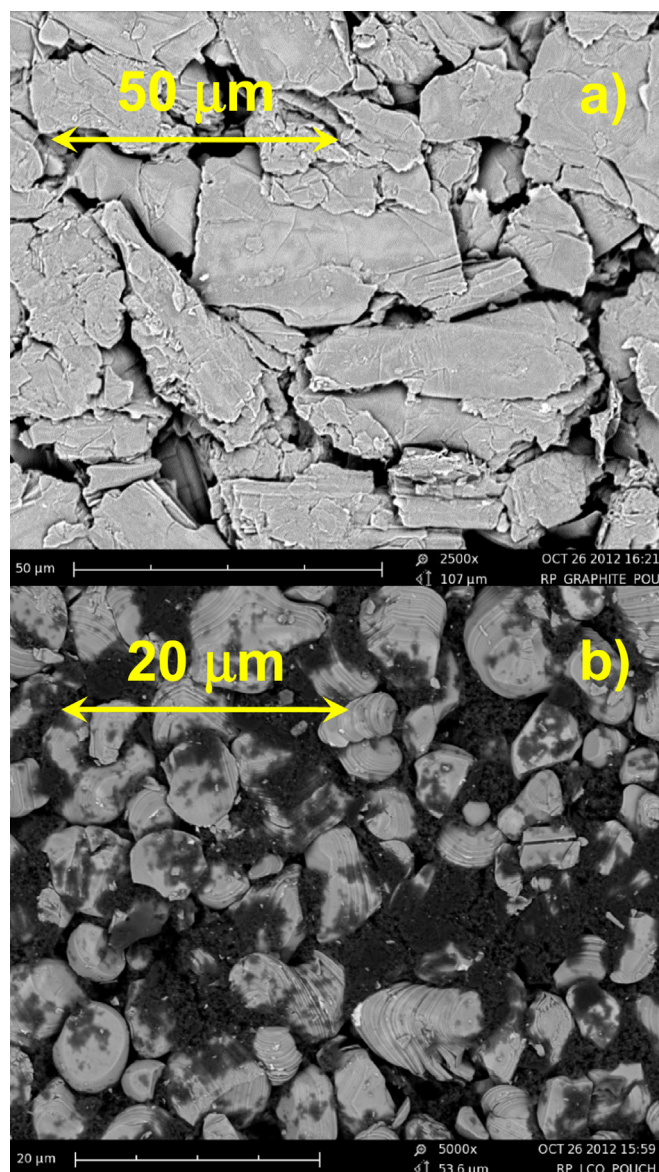


Fig. 1. SEM images of the surface of: a) the graphite negative electrode and b) the LiCoO₂ positive electrode. These images were taken of fresh electrodes taken from dry cells. Carbon black can be observed in the LiCoO₂ electrode.

additives. In cases where additives yielded promising results, a series of experiments where an additive's concentration was increased stepwise (e.g. 0.5, 1, 2, 4 and 6 wt.%) were performed. Duplicate cells were made in all cases to ensure the repeatability of results. The results reported are the average for the two cells and the error bars give the difference between the results for the two cells.

Several of the dry pouch cells were used to determine the water content in the pouch cell electrodes. A Mettler-Toledo C30 Karl-Fischer analyser equipped with a heated oven was used to evaporate the water from the electrodes into the titrator. The sum of the water contents found in the negative (330 ± 30 ppm) and positive electrodes (640 ± 70 ppm), respectively, would correspond to a level of 1100 ppm water by mass in the electrolyte.

After filling with 0.75 g of electrolyte and vacuum sealing (MTI Corporation, MSK-115A) in an argon-filled glove box, a centrifugal wetting (50 g-force for 20 min) procedure and a 24 h hold at 40.0 ± 0.1 °C and 1.5 V were used to ensure complete wetting of the cell coil. The first charge–discharge cycle (called the formation process here) was charging at 2 mA for the first 10 h then at 15 mA for the rest of the charge to 4.2 V. The cells were then discharged to 3.775 V at 15 mA. Following the formation process, cells were degassed in the glove box and vacuum sealed again.

The cells were cycled using the UHPC between 2.8 and 4.2 V at 40.0 ± 0.1 °C using currents corresponding to C/15 for 15 cycles where comparisons were made. After the UHPC cycling, electrochemical impedance spectroscopy (Bio-Logic VMP3), with a 10 mV perturbation and a frequency range from 10 mHz to 100 kHz, was used to measure the combined charge transfer resistance (R_{ct}) of both electrodes in each cell. Before the impedance tests, cells were charged to 3.8 V on the Maccor 4000 series charger and held at 3.8 V until the current dropped below the corresponding C/1000 current, so that all cells were measured under the same conditions. All impedance data were collected at 10.0 ± 0.1 °C, not room temperature, in order to separate the impacts of the various additives better.

3. Results and discussion

Fig. 2 shows the voltage of a LiCoO₂/graphite pouch cell versus absolute capacity for the first fifteen cycles of testing. This cell had 1 M LiPF₆ EC:EMC electrolyte with no additives. The data was collected using the high precision charger so the shift of the capacity to higher and higher values with each cycle is real and is

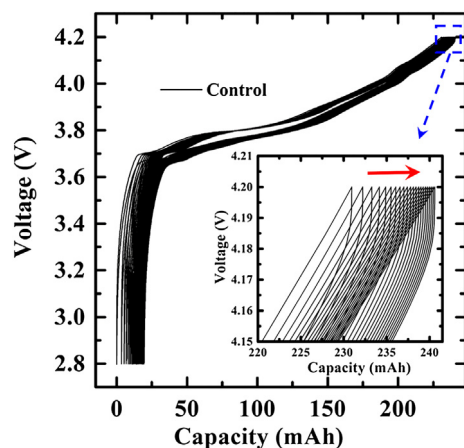


Fig. 2. Cell voltage versus cell capacity for 15 consecutive cycles of a LiCoO₂/graphite cell measured with the high precision charger. The inset shows how the charge endpoint capacity slips to larger and larger capacity each cycle.

caused by electrolyte oxidation at the positive electrode. The inset graph in Fig. 2 shows the data collected very near the top of charge during each cycle to highlight what we mean by the “charge endpoint capacity”. The charge endpoint capacity increases or “slips” to higher capacity with every cycle. The purpose of Fig. 2 is to define what is meant by charge endpoint capacity slippage.

Coulombic efficiency (CE), charge endpoint capacity slippage and R_{ct} are three important parameters to measure in order to quantify the impact of additives on Li-ion cells. One generally desires a high CE, a low charge endpoint capacity slippage and a small R_{ct} . Fig. 3 shows typical CE vs cycle number, charge endpoint capacity vs cycle number (to determine the charge slippage rate), and Nyquist plots (to determine R_{ct}) for LiCoO₂/graphite pouch cells with several selected electrolyte additives added singly or in combination. Fig. 3 is presented as an introductory plot to explain how CE, charge slippage and R_{ct} were calculated in this study. The vertical dashed lines in Fig. 3a indicates that the CE was calculated as the average of the values between cycles 13 and 15. In the CE comparison graph of all the additives (Fig. 6) we chose to plot the quantity “(1 – CE)/(time of one cycle)” so that small variations in cell capacity can be eliminated [17] and so that these measurements can be directly compared to data collected at other C-rates. In this paper “(1 – CE)/(time of one cycle)” is called the coulombic inefficiency per hour or CIE/h. The solid black line in Fig. 3b is a fitted line to the charge endpoint capacity versus cycle number plot for cycles 11 to 15. The charge slippage is taken as the slope of this line in mAh per cycle. R_{ct} , as marked in Fig. 3e, was taken to be the diameter of the overlapping semicircles from the Nyquist plots. Fig. 3 shows that cells with 2 wt.% VC added to the electrolyte show a good combination of properties and therefore it is useful to compare all other cells to the control cells and also to the 2 wt.% VC cells.

Fig. 4 shows representative discharge capacity versus cycle number (Fig. 4a) and voltage versus capacity (Fig. 4b) for LiCoO₂/graphite pouch cells with several selected electrolyte additives as indicated. Fig. 4 is presented as another introductory plot to show representative data for these pouch cells. Fig. 4a illustrates the difficulty in assessing which additives are best based only on short-term capacity versus cycle number graphs. Fig. 4a shows that apart from two cells, 10 of the 12 cells plotted have capacities within $\pm 2\%$. One cell (with 2% VC + 2% VEC + 2% FEC) has about 15 mAh capacity lower than the other cells which may indicate a wetting problem for that cell. Nevertheless, the CE and charge endpoint capacity slippage for the pair of 2% VC + 2% VEC + 2% FEC cells agree well. Fig. 4b shows the voltage versus capacity for the 16 cycles of the cells containing 2% VC + 1% LiBOB. The voltage–capacity curve continually slips to the right as cycling proceeds and the charge endpoint capacity slippage rate is 0.15 mAh/cycle during cycles 11–15.

The experiments described here were all made using the same pouch cells but were made over a period of many months due to the availability of UHPC equipment which is in great demand. In order to be sure that there were no systematic drifts in CE with time over these months, due to variations in electrolyte, for example, control pouch cells were made in each sub-experiment. Fig. 5 shows a “run chart” of the CIE/h of separate batches of control pouch cells plotted versus their assembly date. Fig. 5 shows that the variation in the control cells is very small, so we are confident that the results presented below are reliable.

Fig. 6 shows the results of CIE/h for all the cells tested in this study. Fig. 6a shows the results grouped by color code according to sub-experiments, for example, where the amount of LiBOB additive was varied, etc. Fig. 6b shows the results ordered from the “best” (the smallest value of CIE/h) to the “worst”. The horizontal black dashed lines in Fig. 6 were drawn at the level of CIE/h for the control

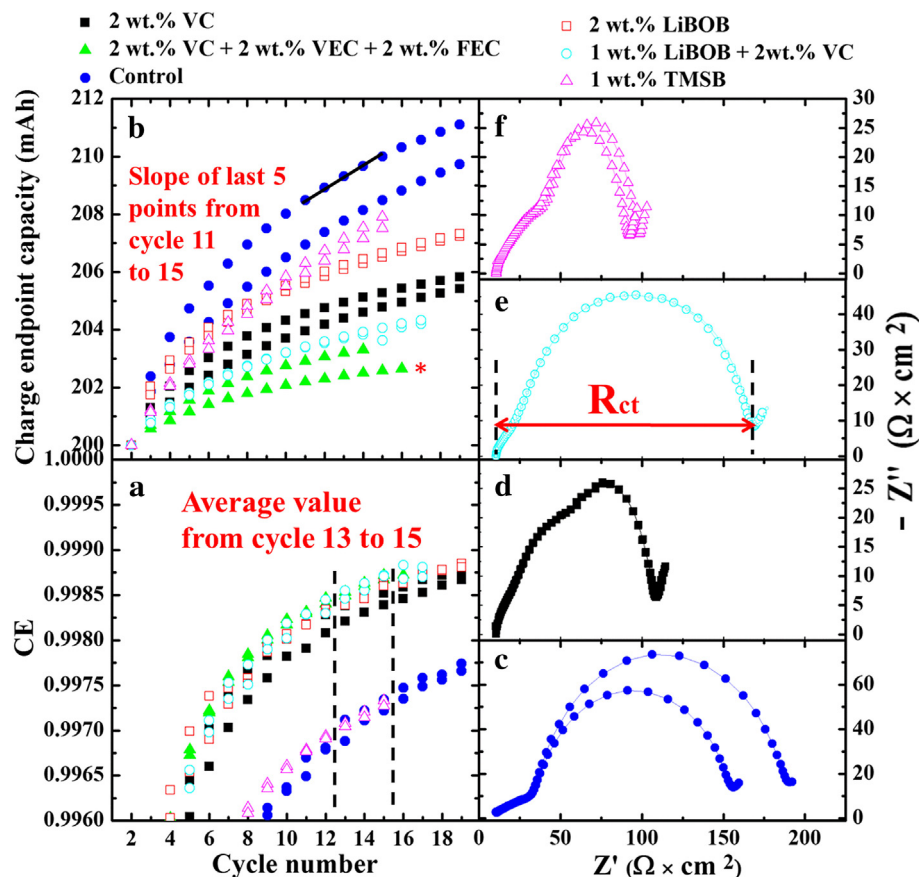


Fig. 3. (a) CE and (b) charge endpoint capacity versus cycle number and (c–f) Nyquist plots for LiCoO₂/graphite pouch cells with different electrolyte additives as indicated. (Cells indicated by a “*” may have a wetting problem).

cells and for the “best” cells. The purple dashed line in Fig. 6 was drawn at the level of CIE/h for the cells with 2 wt.% VC. In order for additives to be better than 2 wt.% VC, they should fall below the purple dashed line.

Fig. 6a shows some interesting trends for the sub-experiments. Adding VC, FEC or LiBOB to the control electrolyte initially decreases the CIE/h. For VC and FEC, the levels at 4 and 6 wt.% are slightly higher than the levels at 2 wt.%. The levels for 4 and 6 wt.%

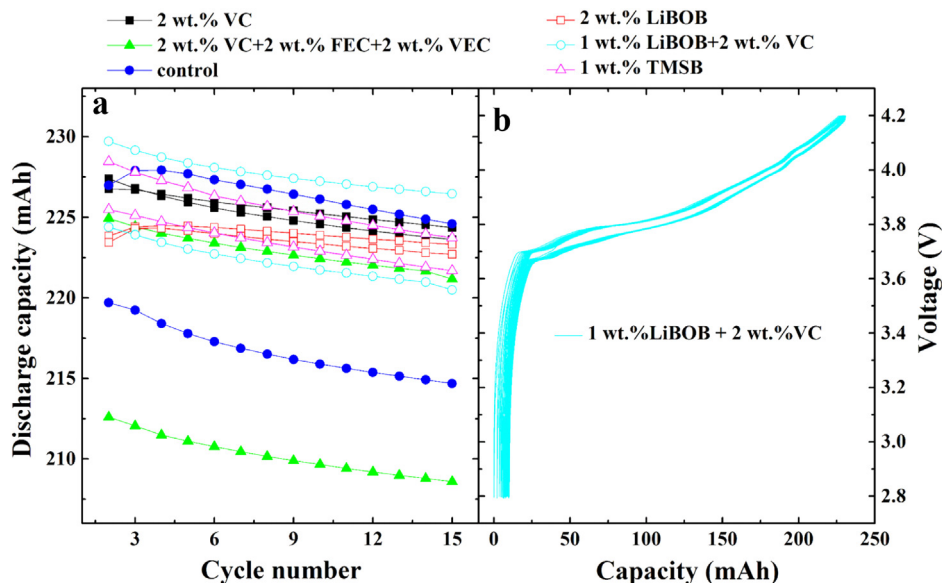


Fig. 4. (a) Discharge capacity versus cycle number and (b) voltage versus capacity for LiCoO₂/graphite pouch cells with different electrolyte additives as indicated. (Cells indicated by a “*” may have a wetting problem).

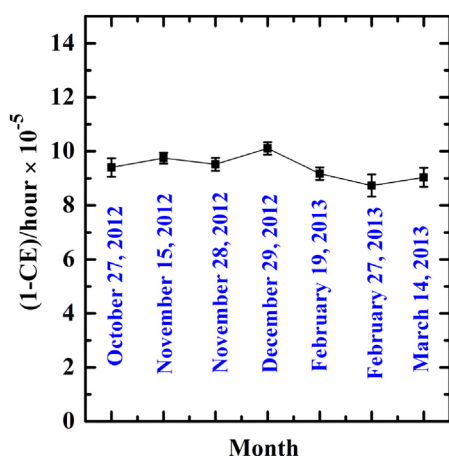


Fig. 5. Columbic inefficiency (1 – CE) per hour (CIE/h) for separate batches of control pouch cells versus the assembly date.

LiBOB are much higher than 2 wt.% of those additives. Fig. 6a shows that cells with VC alone, FEC alone and LiBOB alone gave lower CIE/h than control cells. Cells with 1 or 2 wt.% VC alone and LiBOB alone showed similarly low CIE/h.

Cells with either TMOBX alone or VEC alone demonstrated higher CIE/h than the control cell. Readers may feel that TMOBX and VEC are useless additives. However, that may not be the case. Additives added in combination can show better performance than additives added singly. For instance, when 0.5 or 1 wt.% VEC was added together with 1 wt.% LiBOB, cells exhibited even lower CIE/h than cells with VEC alone or LiBOB alone. Cells with the combination of 1 or 2 wt.% VC with 1 wt.% LiBOB demonstrate even lower CIE/h than cells with VC alone and LiBOB alone. Nevertheless, when TMOBX was used together with either VC and/or LiBOB, cells only showed lower CIE/h than cells with TMOBX alone, but higher CIE/h than cells with VC alone or LiBOB alone, indicating that TMOBX does not help improve the CE of lithium-ion cells in agreement with reference [10]. Moreover, cells with additives of 2 wt.% VC, 2 wt.% VEC and/or 2 wt.% FEC in combination showed similar or lower CIE/h than the cell with 2 wt.% VC.

Cells with TMSB alone, TtBB alone, TBB alone, TMB alone, TiPB alone and TEB alone all showed higher CIE/h than the control cell. When 2 wt.% VC was added together with these additives, most of the cells still showed higher CIE/h than the control cells, indicating the poor performance of these additives on CE.

Fig. 6b shows the CIE/h of the various cells plotted from the “best” (left side) to the “worst” (right side). The cell containing 2 wt.% FEC, 2 wt.% VC and 2 wt.% VEC shows the lowest CIE/h among

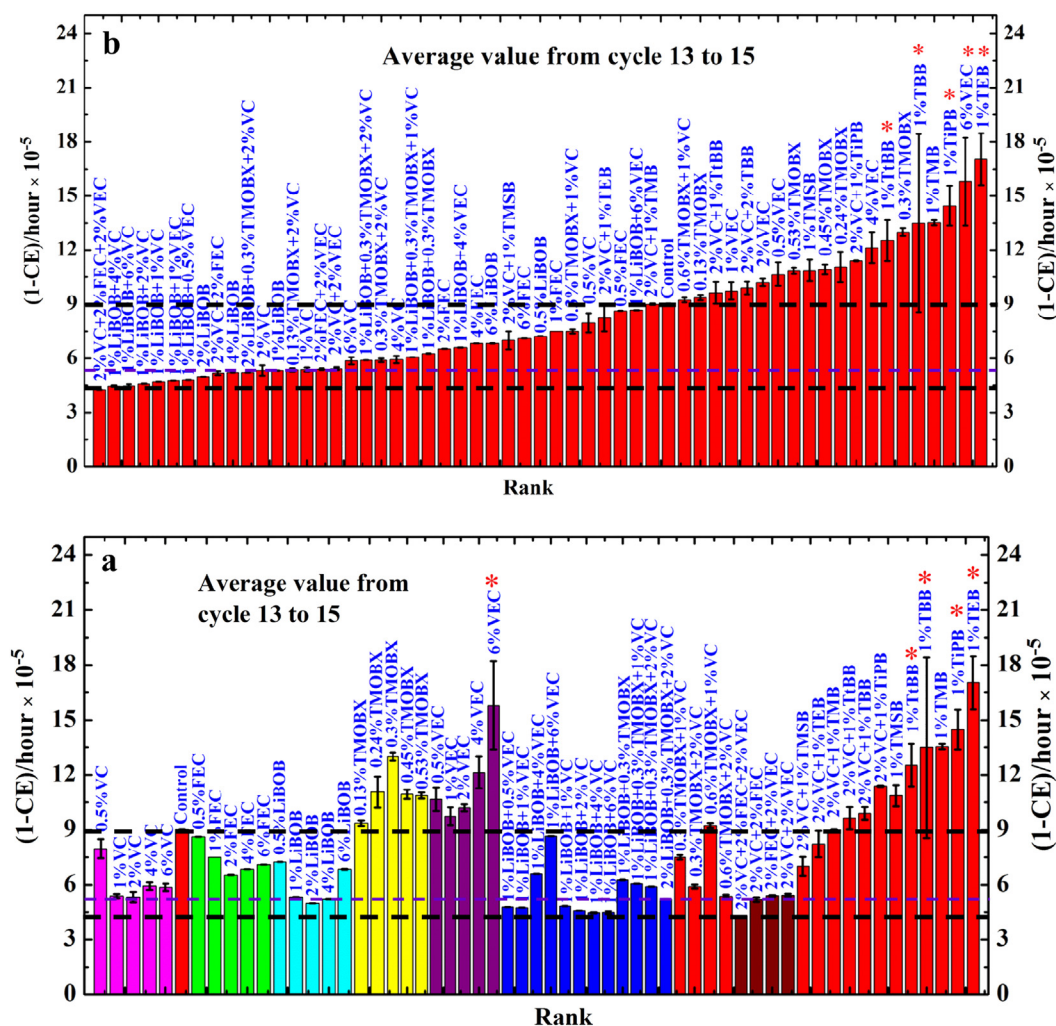


Fig. 6. Columbic inefficiency (1 – CE) per hour (CIE/h): (a) grouped by sub-experiment (color coded) and (b) ranked from the “best” (left) to “worst” (right), for LiCoO₂/graphite pouch cells with different electrolyte additives used singly or in combinations. (*) – Cells developed a large amount of gas during formation and exhibited small cycling capacities. Data for those cells are reported but are not reliable. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

all the additives studied in this paper. When 1 wt.% LiBOB was added together with either VC (1 or 2 wt.%) or VEC (0.5 or 1 wt.%), cells also demonstrated lower CIE/h than the cells with 2 wt.% VC. We do not understand the reasons for these synergies.

The charge endpoint capacity slippage [18] is another important parameter that should be minimized to obtain cells with the longest lifetime. Fig. 7 shows the charge endpoint capacity slippage, fitted from the corresponding charge endpoint capacity vs cycle number plots as shown in Fig. 3b, for all the cells with the different additives. Fig. 7a shows the results grouped by sub-experiment and Fig. 7b shows the results ordered from the “best” (left side) to the “worst” (right side).

Fig. 7a shows that cells with VC alone, FEC alone and LiBOB alone all have smaller charge slippages than the control cells. However, cells with TMOBX alone and VEC alone had higher charge slippages than the control cells. Likewise, when TMOBX or VEC was added together with either VC and/or LiBOB, the charge slippages of cells decreased but was still larger than the cells with 2 wt.% VC. Cells

with TMSB, TtBB, TBB, TMB, TiPB or TEB did not give promising charge slippages. Most of the additives either singly or in combination show larger charge slippages than the cell with 2 wt.% VC.

Fig. 7b shows the charge slippage ranked from the “best” (left) to the “worst” (right). Cells with 6 wt.% VC alone and additive combinations of 2 wt.% VC, 2 wt.% VEC and 2 wt. % FEC exhibited lower charge slippages than the cell with 2 wt.% VC. The results for 2 wt.% and 6 wt.% VC agree with prior work on NMC/graphite cells [19]. However, the use of greater percentages of additives could increase the charge transfer resistance, which will be considered next.

Fig. 8a shows the results for the charge transfer resistance, R_{ct} , grouped by sub-experiment and Fig. 8b shows the results ordered from the “best” (left) to the “worst” (right). Fig. 8 shows that cells with 6 wt.% VC alone or additive combinations of 2 wt.% VC, 2 wt.% VEC and 2 wt.% FEC show much larger R_{ct} than the cell with 2 wt.% VC, indicating that, in the case of these additives, more additives not only reduce the charge slippage but also increase the

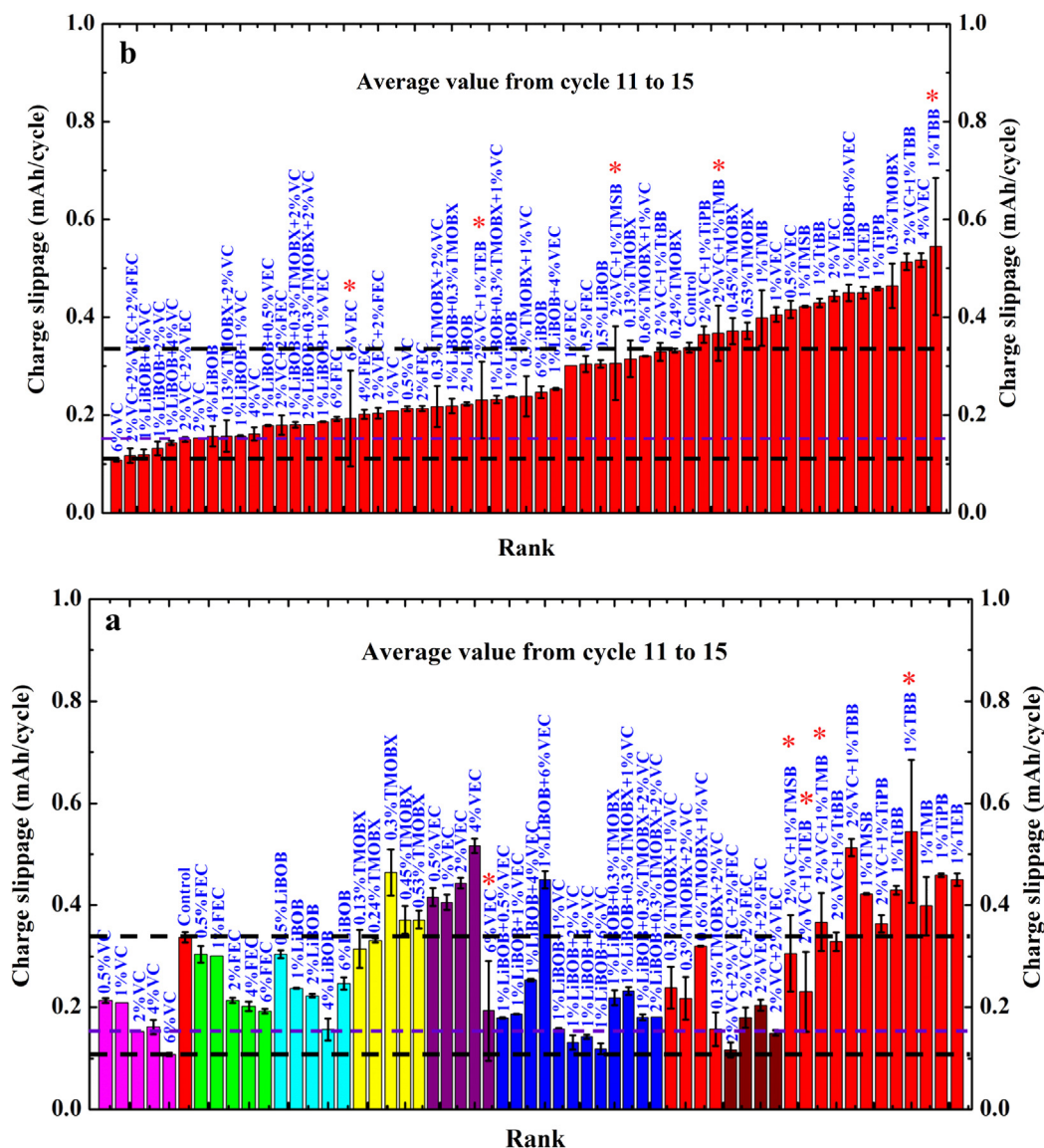


Fig. 7. Charge endpoint capacity slippage rates: (a) grouped by sub-experiment (color coded) and (b) ranked from “best” (left) to “worst” (right), for LiCoO₂/graphite pouch cells with different electrolyte additives used singly or in combinations. (* – Cells developed a large amount of gas during formation and exhibited small cycling capacities. Data for those cells are reported but are not reliable). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

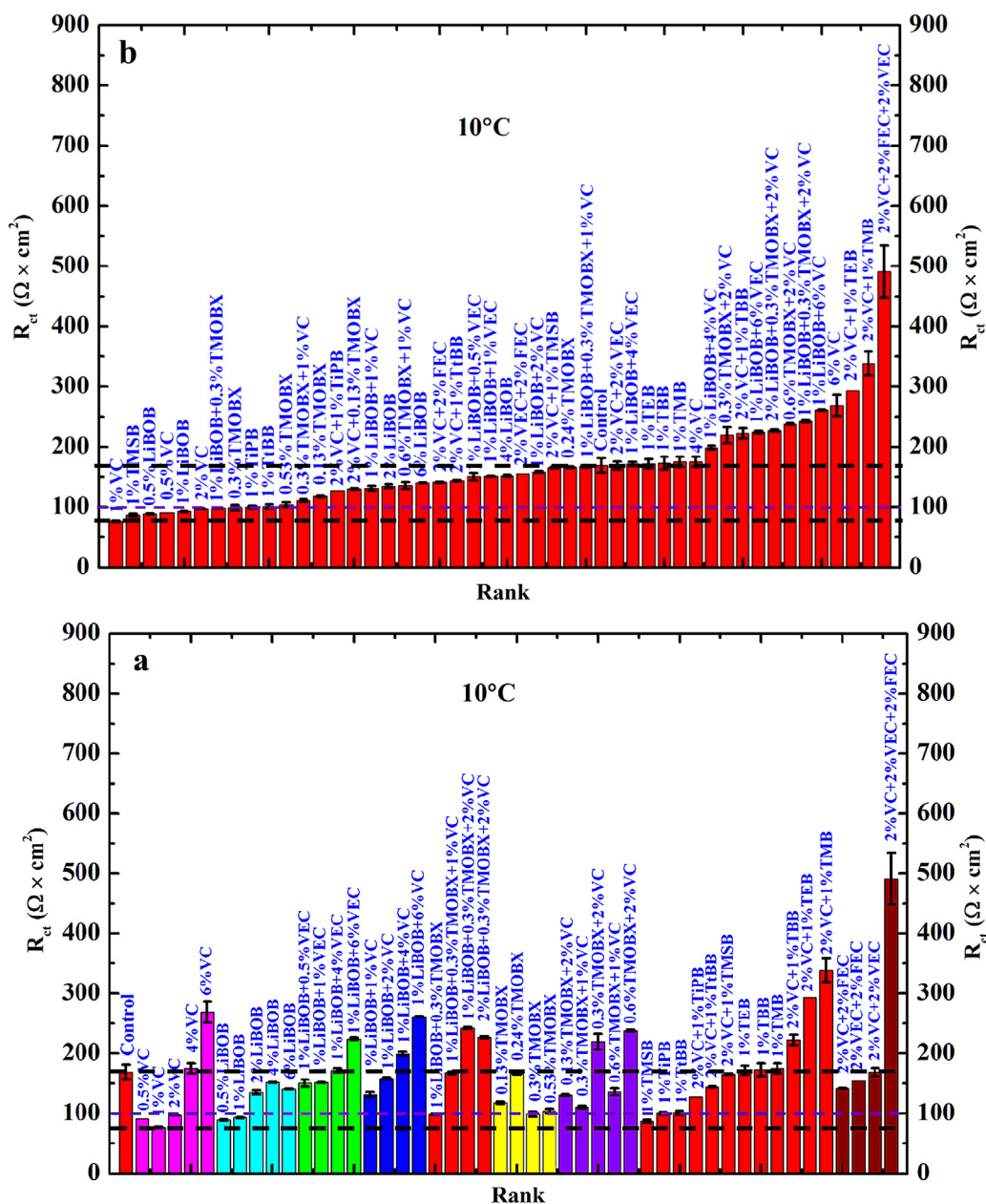


Fig. 8. Charge transfer resistance, R_{ct} , (a) grouped by sub-experiment (color coded) and (b) ranked from “best” (left) to “worst” (right), for LiCoO₂/graphite pouch cells with different electrolyte additives used singly or in combinations. (* – Cells developed a large amount of gas during formation and exhibited small cycling capacities. Data for those cells are reported but are not reliable). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

impedance. We recently showed that the impedance increase from 2 wt.% VC to 6 wt.% VC is caused by an impedance increase at the graphite electrode, not at the LCO electrode [19]. Fig. 8b shows that most of the cells with more than 2 wt. % (total) of additives have R_{ct} values that place them to the right side (bad) of the chart. Fig. 8b also shows that cells with less than 2 wt.% VC alone and less than 1 wt.% LiBOB alone exhibited low R_{ct} . Figs. 6 and 7 show that cells with these additives also demonstrated low CIE/h and low charge slippage. Therefore, LiBOB and VC are promising additives when added singly. Cells with additive combinations of 1 wt.% LiBOB and 1 or 2 wt.% VC also showed a good combination of low CIE/h, low charge slippage and small R_{ct} .

Our previous results showed that TMOBX was an impedance reducer [10,20], which is in good agreement with the results in Fig. 8. However, due to its poor performance in CE and charge

slippage, it should be not added alone. However, the combination of TMOBX with VC and/or LiBOB did not show lower R_{ct} than cells with LiBOB alone, VC alone or TMOBX alone in the cells tested here. Cells with TMSB, TtBB and TiPB show low R_{ct} , while cells with TEB, TBB and TMB exhibit relatively large R_{ct} . However, their combination with 2 wt.% VC increases R_{ct} .

Fig. 8b shows that VC (not more than 2 wt.%) and LiBOB (not more than 1 wt.%) are good impedance reducers, and their combination with other well-known additives studied in this paper still show acceptable R_{ct} compared to the control cells.

4. Conclusions

A systematic study using UHPC and EIS of the effectiveness of different electrolyte additives in LiCoO₂/graphite pouch cells was

presented in this paper. The results for cells with 2 wt.% VC can be used as a baseline to evaluate the effectiveness of different additives for the LiCoO₂/graphite pouch cells. The influences of different electrolyte additives singly or in combination were compared with each other and with the new baseline in terms of CIE/h, charge slippage and R_{ct} . LiBOB and VC were showed to be promising electrolyte additives either used singly or in combination. The combination of 2 wt.% VC, 2 wt.% VEC and 2 wt.% FEC was shown to have the lowest CIE/h and the second lowest charge slippage. Unfortunately, it also had the highest impedance. However, it may be suitable for cells destined only for low rate, long lifetime applications, for example.

The electrolyte additives studied in this work, apart from the borates, are well known. By comparing the results for the borates to the results for VC and LiBOB, it is our opinion that further work on these borate additives is not warranted. This logic represents our search strategy going forward. When additives used singly or in combination with VC and/or LiBOB show better performance (in terms of CIE/h, slippage and R_{ct}) than 2 wt.% VC alone, then such additives will be selected for further in-depth studies, using surface science tools, to determine how they function.

Obviously it would be reassuring to have long-term cycle life testing for all the additive combinations reported here to be sure that the results of the short-term testing mirror the long-term results. Our prior work shows that the correlation between the short term tests and the long term cycling results is generally robust although there have been some exceptions. However, we do not have the resources to carry out vast amounts of long-term testing which does not necessarily measure the impact of additives on reducing parasitic reactions within cells which is what the UHPC experiments measure. We invite university researchers, electrolyte vendors and additive producers to supply their best additives for us to evaluate using the methods presented here and to help us extend the bar charts in Figs. 6–8. A similar study of a wide variety of additives in NMC/graphite cells is now underway.

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References

- [1] M. Broussely, P. Biensan, F. Bonhomme, P. Blanchard, S. Herreyre, K. Nechev, R.J. Staniewicz, *J. Power Sources* 146 (2005) 90.
- [2] G. Jain, in: 30th International Seminar on Primary and Secondary Li Batteries, Ft. Lauderdale, FL, March 11–14, 2013.
- [3] T.B. Reddy, *Linden's Handbook of Batteries*, fourth ed., The McGraw-Hill Companies, Inc., New York, 2010.
- [4] S.S. Zhang, *J. Power Sources* 162 (2006) 1379.
- [5] K. Xu, *Chem. Rev.* 104 (2004) 4303.
- [6] B. Simon, J.-P. Boeue, U.S. Patent No. 5626981, (6 May 1997).
- [7] D. Aurbach, K. Gamolsky, B. Markovsky, Y. Gofer, M. Schmidt, U. Heider, *Electrochim. Acta* 47 (2002) 1423.
- [8] I.A. Profatilova, S.-S. Kim, N.-S. Choi, *Electrochim. Acta* 54 (2009) 4445.
- [9] W. Lu, Z. Chen, H. Joachin, J. Prakash, J. Liu, K. Amine, *J. Power Sources* 163 (2007) 1074.
- [10] J.C. Burns, N.N. Sinha, G. Jain, H. Ye, C.M. VanElzen, W.M. Lamanna, A. Xiao, E. Scott, J. Choi, J.R. Dahn, *J. Electrochem. Soc.* 159 (2012) A1105.
- [11] J.C. Burns, N.N. Sinha, D.J. Coyle, G. Jain, C.M. VanElzen, W.M. Lamanna, A. Xiao, E. Scott, J.P. Gardner, J.R. Dahn, *J. Electrochem. Soc.* 159 (2012) A85.
- [12] J.C. Burns, N.N. Sinha, G. Jain, H. Ye, C.M. VanElzen, W.M. Lamanna, A. Xiao, E. Scott, J. Choi, J.R. Dahn, *J. Electrochem. Soc.* 159 (2012) A1095.
- [13] A.J. Smith, J.C. Burns, S. Trussler, J.R. Dahn, *J. Electrochem. Soc.* 157 (2010) A196.
- [14] T.M. Bond, J.C. Burns, D.A. Stevens, H.M. Dahn, J.R. Dahn, *J. Electrochem. Soc.* 160 (2013) A521.
- [15] J.C. Burns, Adil Kassam, N.N. Sinha, L.E. Downie, Lucie Solnickova, B.M. Way, J.R. Dahn, *J. Electrochem. Soc.* 160 (2013) A1451.
- [16] G. Ceder, *Mater. Res. Soc. Bull.* 35 (2010) 693.
- [17] A.J. Smith, H.M. Dahn, J.C. Burns, J.R. Dahn, *J. Electrochem. Soc.* 159 (2012) A705.
- [18] J. Christensen, J. Newman, *J. Electrochem. Soc.* 152 (2005) A818.
- [19] J.C. Burns, R. Petibon, K.J. Nelson, N.N. Sinha, Adil Kassam, B.M. Way, J.R. Dahn, *J. Electrochem. Soc.* 160 (2013) A1668.
- [20] R. Petibon, C.P. Aiken, N.N. Sinha, J.C. Burns, H. Ye, C.M. VanElzen, G. Jain, S. Trussler, J.R. Dahn, *J. Electrochem. Soc.* 160 (2012) A117.